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13. ABSTRACT (Maximum 200 words) A novel class of second-order nonlinear optical (NLO) side-chain polymer: side-chain polyquinolines was developed. The synthetic approach includes the synthesis of chromophore precursor-containing bis(ketomethylene) monomers and bis(ortho-aminoketone) monomers, the polymerization of the two monomers, and post-tricyanovinylolation to activate the side-chain chromophores of the polyquinolines. The synthesized NLO side-chain polyquinolines possess high glass transition temperature, good thermal stability, and processibility. The testing results show that the NLO side-chain polyquinolines exhibit a large electro-optical coefficient (r_{33}) value (up to 17 pm/V measured at 0.63 μ m, and 9 pm/V at 0.83 μ m), and temporal stability of dipole alignment at 100°C for more than 500 hours. DTIC QUALITY INSPECTED 5			
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FINAL TECHNICAL REPORT

15 Aug., 1994 - 14 Aug., 1995

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FINAL TECHNICAL REPORT

1. OBJECTIVES OF THE RESEARCH EFFORT

Recent scientific reports have shown great improvements and promising results in the development of high-speed light modulators and switches based on the second-order nonlinear optical (NLO) polymers. The challenges to achieving useful NLO polymeric material systems for practical devices are still based on resolving of the following key issues: the electrooptical (E-O) coefficients of the systems must be large enough to accommodate the operating voltage of the devices; they must retain a significant fraction of their initial values at continuous operating temperatures of approximately 80°C and during short exposure to temperatures >250°C; the material systems must possess good mechanical properties for multilayer processing; and low optical attenuation. The main objective of the research activity of this program is to design and synthesize highly efficient NLO polyquinolines possessing high E-O coefficient (r_{33}), good processibility, and high temperature alignment stability of the poled NLO chromophores. The general approaches include the incorporation of highly efficient and thermally stable aromatic NLO chromophores into the backbone of high performance polyquinolines.

2. STATUS OF THE RESEARCH EFFORT

2.1 Background of the Research

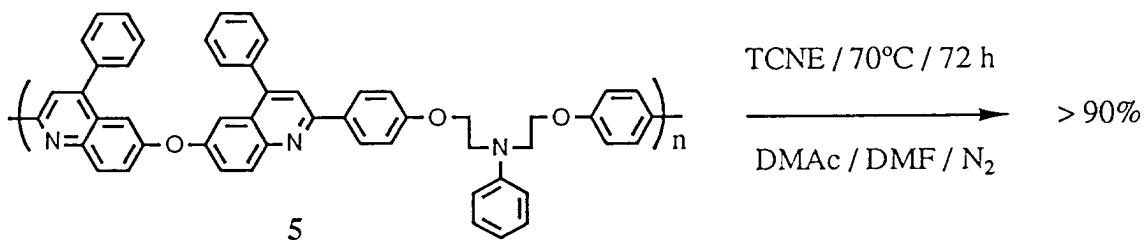
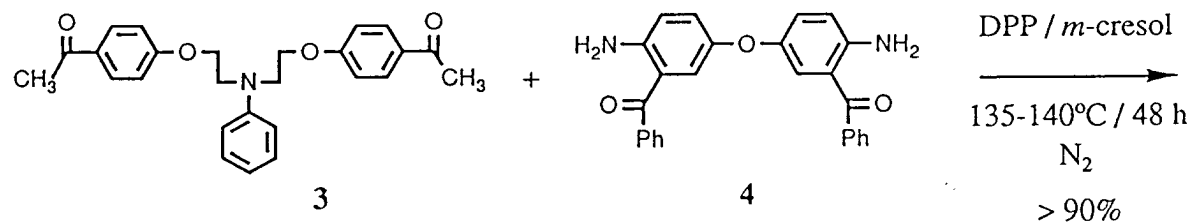
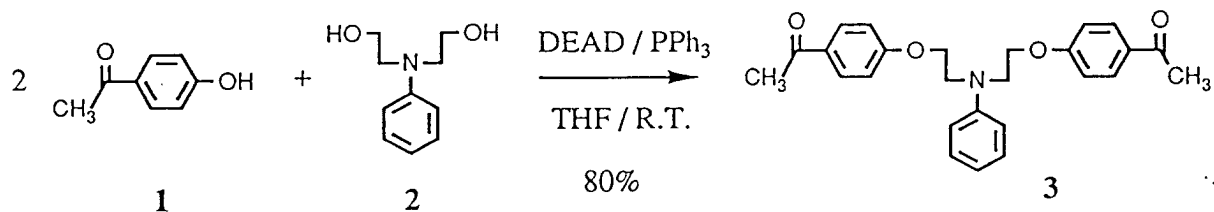
To date, polyimides were considered to be the most attractive host candidates for the development of high temperature NLO polymers. In particular, the NLO side-chain or crosslinked polyimides were considered to be the most promising systems among different NLO polyimides. Although the results reported for these NLO polyimides are

quite encouraging, there are some deficiencies, such as a highly reactive environment during the imidization process, which severely limits the selection of usable chromophores. Recently, we have reported achieving very high electro-optical coefficient ($r_{33} = 45 \text{ pm/V}$ at $1.3 \text{ }\mu\text{m}$) and long-term temporal stability of E-O signal at 80°C for more than 2500 hrs in a guest/host polyquinoline system. This guest/host polyquinoline polymer provides very promising results, however, there is a strong need to further improve their mechanical properties (for multilayer integration) and thermal stability in order to accommodate the processing requirements of E-O devices. Hence, we have been focused on the development of a series of novel functionalized polyquinolines and second-order NLO side-chain polyquinolines. In this technical report, we would like to summarize our research effort on the design and the synthesis of this novel class of side-chain polyquinolines. The testing results of the electro-optical coefficients, thermal stability, temporal stability of the poling-induced dipole moments of the polymer films, and other physical properties of side-chain polyquinolines are also summarized in this report.

2.2 Chemical Aspect of the Research Effort

Our approach to these NLO side-chain polyquinolines includes the synthesis of chromophore precursor-containing bis(ketomethylene) monomers and bis(*ortho*-amino ketone) monomers, the polycondensation of the two monomers, and post-tricyanovinylolation of the polyquinolines to activate the side-chain NLO chromophores (Scheme 1 and 2). The wide variety of monomers and the relatively mild conditions of the quinoline-forming reaction to generate high molecular weight polymers allows the synthesis of a large series of NLO polyquinolines with different polymer backbones (such as aliphatic embedded as shown in Scheme 1 and aromatic polyquinoline as shown in

Scheme 1. Synthesis of Aliphatic imbeded NLO Side-chain Polyquinolines^a



a:

DEAD: diethyl azodicarboxylate

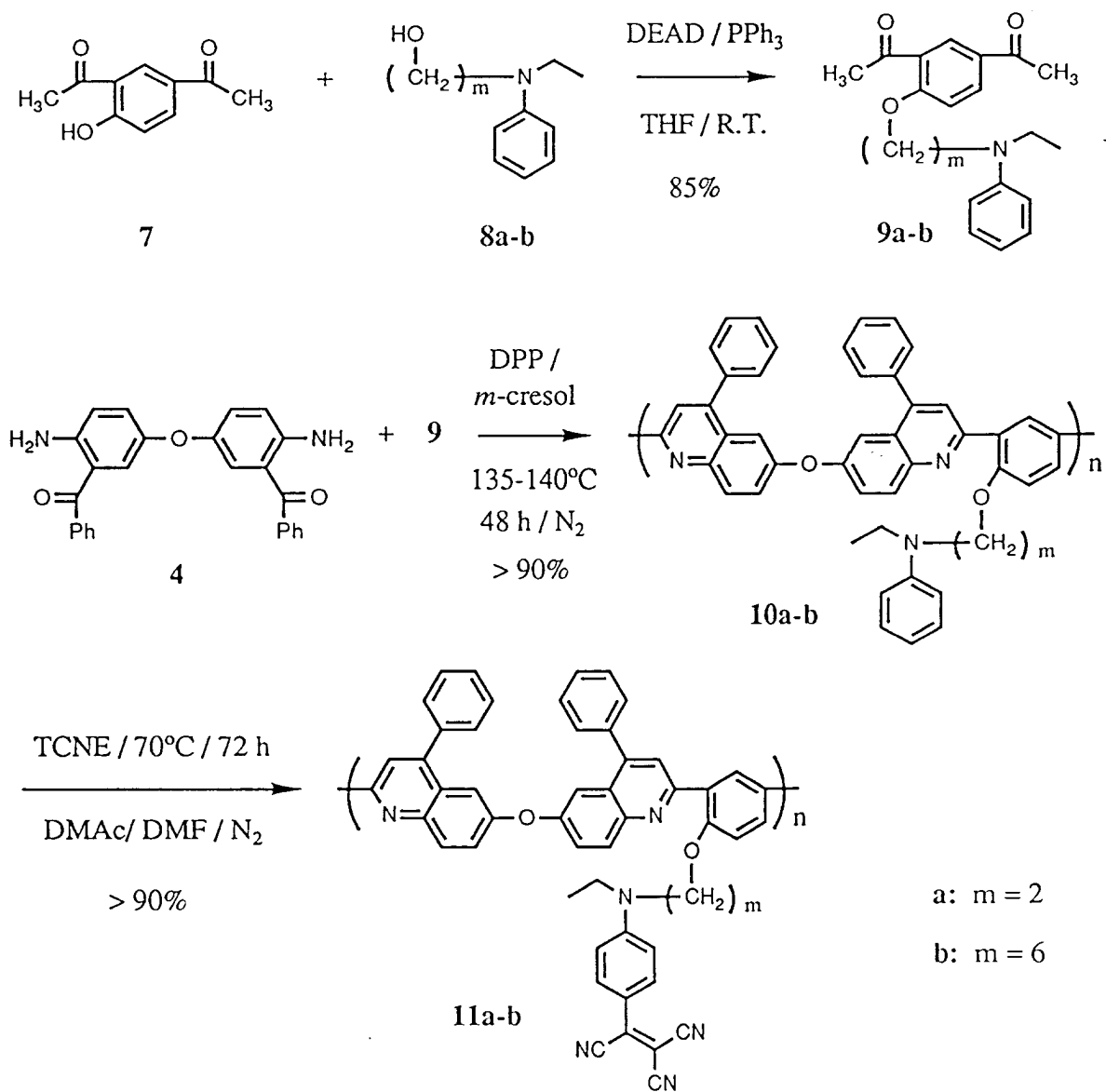
DPP: Diphenyl phosphate

TCNE: tetracyanoethylene

DMAc: *N,N*-dimethylacetamide

DMF: dimethylformamide

Scheme 2. Synthesis of Aromatic NLO Side-chain Polyquinolines



Scheme 2) and different chromophores to fine-tune the physical properties of the polymers.

Polyquinolines, which were first developed by Stille *et al*, represent a class of high performance polymers with outstanding thermal stability (>450°C), low dielectric constants (2.5 - 3.0), low humidity absorption (0.10 - 0.15%), low optical loss, low shrinkage, very high Tg (250 - 400°C), excellent processibility and compatibility with plasma or reactive ion etching. Their mechanical properties, electrical properties, linear optical, and third-order nonlinear optical properties were well established by Stille, and recently by Jenekhe and co-workers. A polyquinoline composition (PQ-100) was recently commercialized by Maxdem Inc. To our knowledge, no studies related to NLO side-chain polyquinolines have been reported prior to this work.

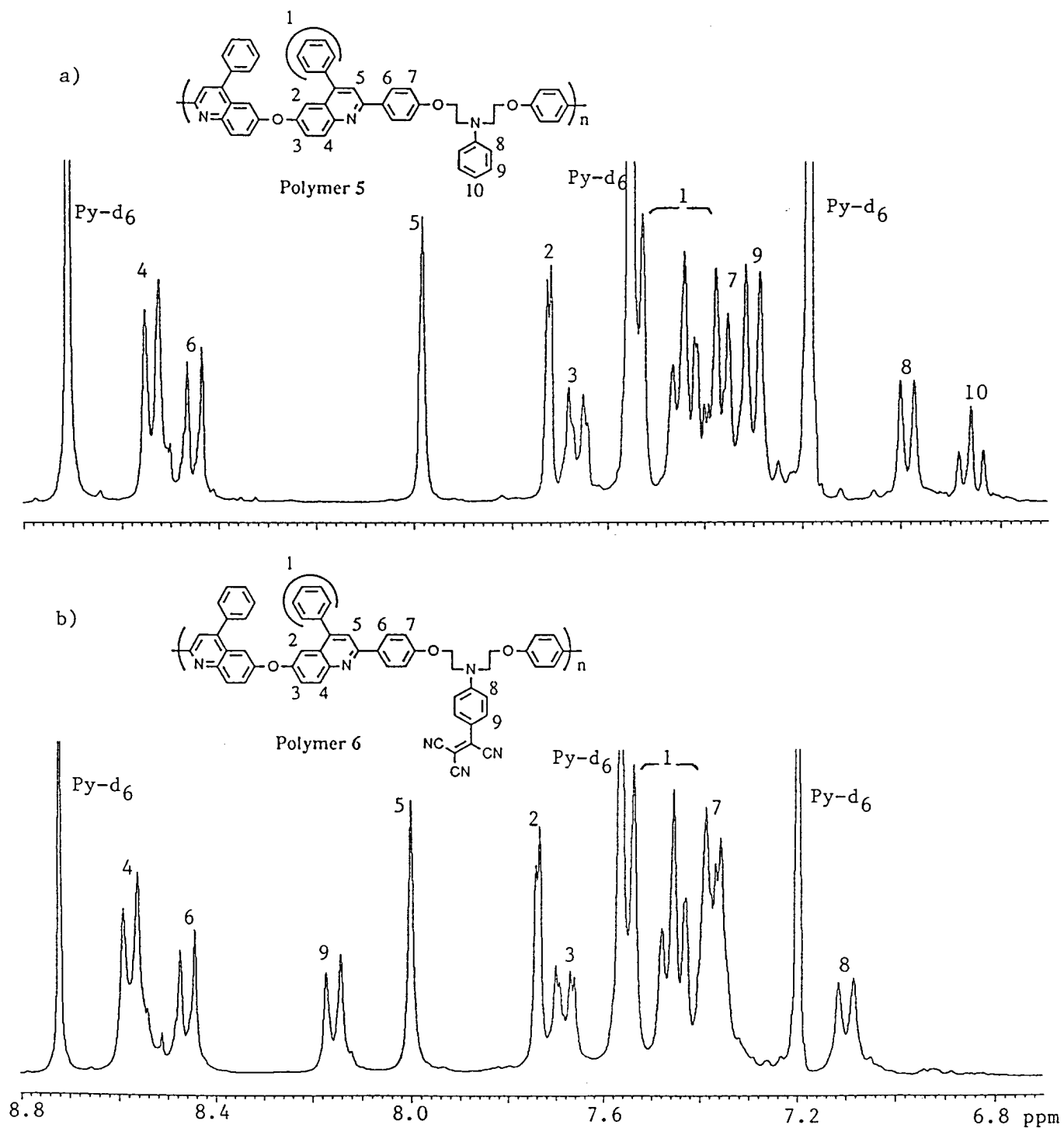
The chromophore precursor-containing bis(ketomethylene) monomers **3**, **9a**, and **9b** were prepared as shown in Schemes 1 and 2. The related starting compound 2,4-diacetylphenol **7** and bis(*ortho*-amino ketone) **4** were synthesized according to the literature methods. The precursor polyquinolines, **5**, **10a**, and **10b**, were synthesized via polymerizations of the ketomethylene and the amino-ketone monomers in diphenyl phosphate/*m*-cresol at 135-140°C for 48 h under nitrogen with a yield of >90%. The NLO side-chain polyquinolines, **6**, **11a**, and **11b**, were prepared by the post-tricyanovinylation of the precursor polyquinolines with tetracyanoethylene (TCNE) in DMAc/DMF at 70°C for 72 h with a yield of >90%. To unambiguously verify the polymer structures shown in Schemes 1 and 2, the polyquinolines were characterized by NMR spectroscopy. Surprisingly, excellent proton resonances and splittings and their correct integration signals can be observed in the ¹H NMR (pyridine-*d*₆) spectra for all the protons in the polymer repeat units (see Figure 1a for polyquinoline **5** for example). The post-tricyanovinylation of the precursor polyquinolines was monitored by proton

NMR spectroscopy. The completion of the tricyanovinylation was also verified by spectroscopy. For example, the three sets of chemical shifts at 6.9 (triplet), 7.0 (doublet), and 7.3 ppm (triplet) were attributed to the protons 10, 8, and 9 of precursor polyquinoline **5** (Figure 1a). The resonance peak for the proton 10 disappeared after the proton was replaced by the tricyanovinyl group, and the protons 8 and 9 were downshifted to 7.1 (doublet) and 8.2 ppm (doublet) after the tricyanovinylation (see Figure 1b for side-chain polyquinoline **6**).

2.3 Physical Aspect of the Research Effort

The precursor polyquinolines **5**, **10** and the side-chain polyquinolines **6**, **11** were all soluble in polar solvents, such as cyclopentanone, cyclohexanone, *N,N*-dimethylacetamide, *m*-cresol, *N*-methylpyrrolidinone, pyridine, and tetrahydrofuran (THF). The precursor polymers **5** and **10** were soluble in chloroform while the side-chain polymers **6** and **11** were only slightly soluble in chloroform. Due to the solubility in THF, the molecular weights of both precursor and side-chain polymers can be estimated by gel permeation chromatography (GPC). Polyquinoline **5**, for example, has a weight average molecular weight $M_w=41000$ with a polydispersity index of 1.90. Polyquinoline **6** has a higher M_w of 46000 and a smaller polydispersity of 1.68 due to the post-tricyanovinylation and the further purification. The UV-vis spectra of thin films of the side-chain polyquinolines exhibited a strong absorption pattern (λ_{max} of 519 nm for polymer **6** and of 530 nm for polymer **11**) due to the $\pi-\pi^*$ charge-transfer band of the NLO chromophore of the *para*-diethylamino-tricyanovinyl benzene. All the resulting side-chain polyquinolines have a high Tg and good thermal stability. Both polymers **6** (chromophore loading level of 27% by weight) and **11b** (loading level of 29%) have a Tg of 175°C, while polymer **11a** has a Tg of 200°C by differential scanning calorimetry

Figure 1. Aromatic region of ^1H NMR (pyridine- d_6) spectra of the precursor
polyquinoline 5 and the side-chain polyquinoline 6



(DSC) analysis. They all have a thermal stability of < 3% weight loss up to 300°C by thermogravimetric analysis (TGA).

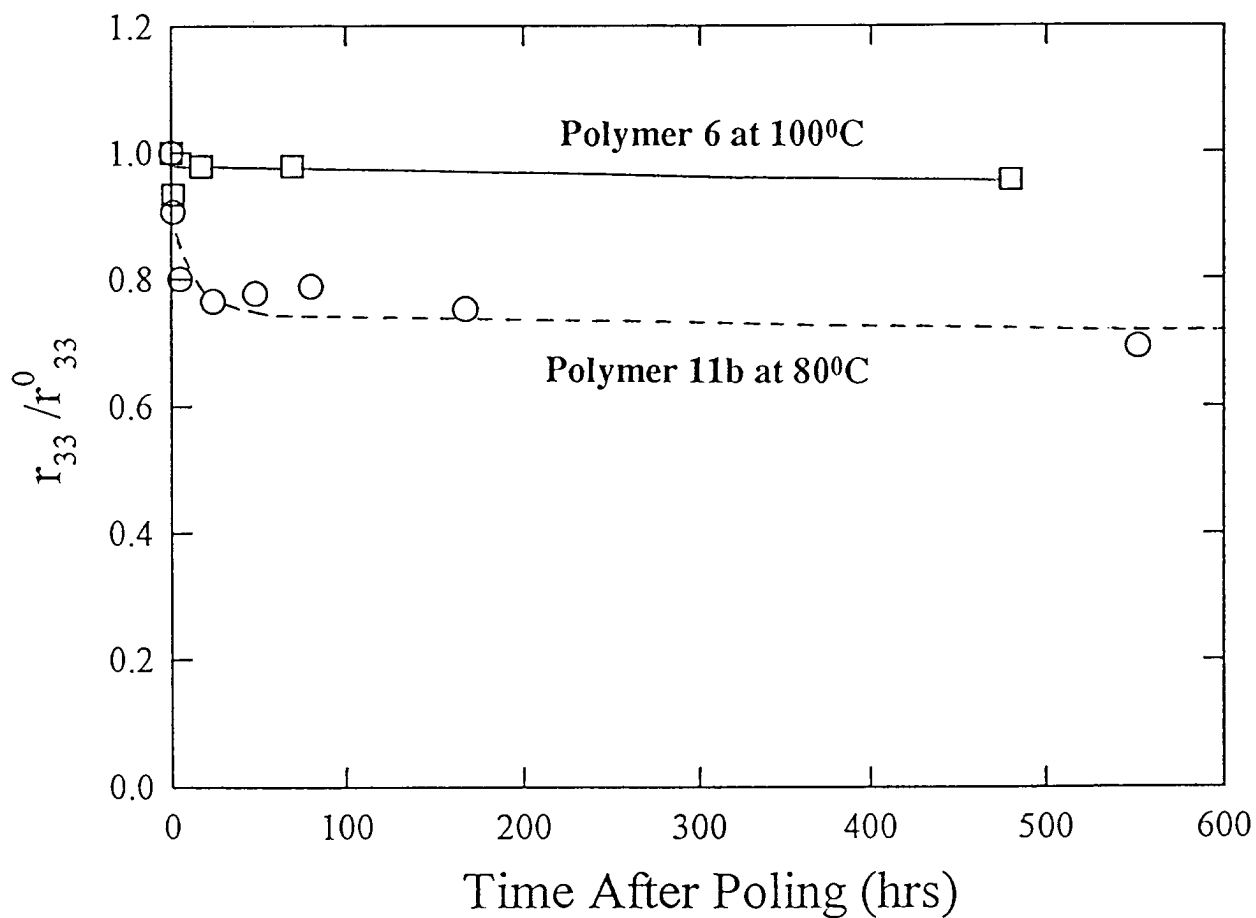
Optical-quality thin films (~1.2 μm) of the polyquinolines **6** and **11** were prepared by spin-coating of the polymer solutions in cyclopentanone (15% m/m solution, filtered through a 0.2 μm syringe filter) onto an indium tin oxide (ITO) glass substrate. The films were kept in a vacuum oven at 120°C over night to ensure the removal of the residual solvent. Dipole alignments in the NLO side-chain polyquinolines can be achieved and the second-order nonlinearity can be induced either by contact poling or corona poling. The E-O coefficient (r_{33}) was measured with an experimental setup similar to that described by Teng *et al.* Polyquinoline **11b**, for example, exhibited a preliminary r_{33} value of 17 pm/V measured at 0.63 μm , and 9 pm/V at 0.83 μm with a poling field of 1.0 MV/cm. Polyquinoline **6** exhibited an r_{33} value of 10 pm/V at 0.63 μm , and 4.5 pm/V at 0.83 μm . The r_{33} value of polymer **6** retained >95% of the original value at 100°C for 500 h, and the r_{33} value of polymer **11b** retained ~80% of the original value at 80°C for more than 500 h (Figure 2). Polyquinoline **6** has a dielectric constant of 3.89 and polyquinoline **11b**, 3.74 calculated from the capacitance of the films measured using an HP 4192A Impedance Analyzer.

In conclusion, we have developed a synthetic methodology for a novel class of second-order NLO side-chain polyquinolines which demonstrates excellent temporal stability of the poling-induced dipole moments of the polymer films at elevated temperatures. This class of side-chain polyquinolines has great flexibility both in backbone structures and in side-chain chromophores for fine-tuning the properties of the polymeric materials. The material system is a potential alternative or a superior substitute for existing systems of polyimide. The synthesis of higher Tg side-chain polyquinolines

and the optimization of their E-O coefficient and thermal alignment stability are continuously in progress.

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Figure 2. Temporal stability of the poled side-chain polyquinoline 6 at 100°C, 11b at 80°C. (Normalized r_{33} as a function of baking time)



3. PUBLICATIONS IN TECHNICAL JOURNALS

- 1) "A Novel Class of Nonlinear Optical Side-Chain Polymer: Polyquinolines with Large Second-Order Nonlinearity and Thermal Stability", T.-A. Chen, A. K-Y. Jen, Y. M. Cai, submitted to *J. Am. Chem. Soc.*.
- 2) "Thermally Stable Poled Polyquinoline Thin Film with Very Large Electro-optical Response", Y. M. Cai, A. K-Y. Jen, *Appl. Phys. Lett.*, **1995**, 67, 299.
- 3) "High Temperature Poled Side-Chain Polyimides for Electro-Optical Application", A. K-Y. Jen, Y. M. Cai, K. J. Drost, Y. J. Liu, V. P. Rao, T.-A. Chen, R. M. Mininni and J. T. Kenney, *Polymeric Material: Science and Engineering* **1995**, 72, 213.
- 4) "The Development of Highly Active, Thermally Stable Chromophores and Polymers for Electro-Optical Applications", A. K-Y. Jen, V. P. Rao, Y. M. Cai, K. J. Drost, Y. J. Liu and J. T. Kenney, Extended abstract, p. 13, 15th International Conference on Polyimide, 1994.
- 5) "High Temperature Poled Side-chain Polyimides and Polyquinolines for Electro-optic Applications", A. K-Y. Jen, Y. M. Cai, T.-A. Chen, V. P. Rao, K. J. Drost, Y. J. Liu, J. T. Kenney, and R. M. Mininni, *International Conference of Advanced Materials-VI*, 1995.
- 6) "Design and Synthesis of Novel Side-chain Polyquinolines and Polyimides for Second-order Nonlinear Optics", A. K.-Y. Jen, T.-A. Chen, Y. Cai, *Proceedings of Materials Research Society* **1995**, in press.